Phase Stability and Electronic Structure of K-Ag Intermetallics at High Pressure

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The very unusual structural features observed in the recently characterized high pressure novel K-Ag alloys can be rationalized using simple electron counting rules and a moment analysis of the electronic density of states. The stability of the alloys is attributed to almost complete electron transfer from K 4*s* bands to Ag 5*s* bands and spatially extended Ag 5*p* bands. This allows for efficient Ag-Ag bonding interactions at an unusually long distance of 5.54 Å and exceptionally short K-K bonds due to reduced repulsive interactions between the K^+ ions. The general principles developed here are applicable to the understanding of the structure and bonding of other high pressure intermetallic alloys. [S0031-9007(99)09218-2]

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The thermodynamic stability of intermetallic phases is generally believed to be governed by Miedema's rules [1,2] which state that alloy formation is favored between elements which have similar valence electron density and a large difference in electronegativity. Alkali metals K, Rb, and Cs are therefore not expected to form alloys with noble and transition metals such as Ag and Ni. However, it is well known that the electronic structure of simple alkali metals can be modified significantly by compression. For example, the group I alkali metals of K, Cs, and Rb may take on the characteristics of a transition metal as a result of the pressured induced $s \rightarrow d$ hybridization [3,4]. At even higher pressures, theoretical calculations also show that Cs IV, which is stable at 4.2 GPa, may be considered as an electride $Cs^+ + e^-$ [5]. Badding and coworkers hypothesized that in order to satisfy Miedema's rules, one may have to compress solid K to achieve an electron density favoring the formation of alloys [6]. This hypothesis was verified recently by the successful high pressure synthesis of novel K-Ni [6] and K-Ni [7] alloys.

K_3Ag crystallizes in the BiF_3 structure type (space group $Fm3m$) with the Ag forming a fcc sublattice and the K occupying both octahedral and tetrahedral sites [7]. A very unusual feature of this structure is the very short nearest neighbor K-K separation of 3.39 Å at 6.4 GPa. This distance is about 10% *shorter* than that observed in the bcc phase of elemental K at the same pressure. On the other hand, the first nearest neighbor distance of 5.54 Å between Ag atoms is exceptionally long. K_2Ag exists in the ω-phase structure type with the Ag atoms lying within the hexagonal planes [7]. The Ag-Ag distance in this plane is also 5.54 Å, identical to that found in the hexagonal planes of the fcc sublattice of K_3Ag. The planes of Ag atoms are stacked along the crystallographic **c** direction in a ...*AAA*... simple hexagonal sequence with an interlayer spacing of 3.605 Å at 6.1 GPa. In this structure, the K atoms are arranged in graphitelike sheets intercalated between the hexagonal Ag sheets. The K-K distance within these graphitelike sheets is 3.13 Å at 6.1 GPa, which is about 18% *shorter* than the closest interatomic distance in elemental K at the same pressure. Furthermore, the closest K-Ag distances are 3.39 Å and 3.62 Å for K_3Ag and K_2Ag, respectively, which are only slightly larger than the sum of the atomic radii of K and Ag of 3.30 Å at 6.4 GPa. On the basis of the structural information it might be conjectured that there are significant K-K and K-Ag bondings but the Ag-Ag interactions play only a minor role in the stabilization of the phases. This interpretation is quite illuminating in view of the fact that in most Zintl intermetallic phases, the interatomic distance between the electron-donating element is often shorter by ~10% than in the elemental form [8]. If the K-Ag alloys are indeed Zintl-type phases [9], this observation suggests that these structures are probably composed of K^+ ions and negatively charged Ag frameworks, i.e., ionic K-K and K-Ag interactions but covalent Ag-Ag interactions. This description is in contradiction to the observed long Ag-Ag bonds.

To resolve this dichotomy, first-principles electronic band structure calculations were performed [10] on K_2Ag (Fig. 1A) and K_3Ag (Fig. 1B) and corresponding hypothetical structures of the Ag sublattice with the K atoms removed, $\square_2Ag$ (Fig. 1C) and $\square_3Ag$ (Fig. 1D). In all cases, the Ag 4*d* orbitals form five completely filled flat bands and do not participate in the bonding. The next higher energy band in all the structures is predominantly Ag 4*s* in character and is completely occupied in the structure containing K. The highly dispersed and partially filled bands near the Fermi level of the K-Ag compounds are largely Ag 4*p* with only a minor K 4*s* component. There is no evidence supporting a K $s \rightarrow d$ hybridization in these compounds. The most striking feature common to the band dispersion diagrams for the corresponding structures of the K-Ag alloys with and without K is that the occupied bands are almost identical below the Fermi level both in terms of the number of bands and, *most importantly,* in the shape of the band dispersion. The similar pattern of band dispersions in the corresponding structures, K_2Ag and $\square_2Ag$, K_3Ag and $\square_3Ag$, indicates that the K atoms do

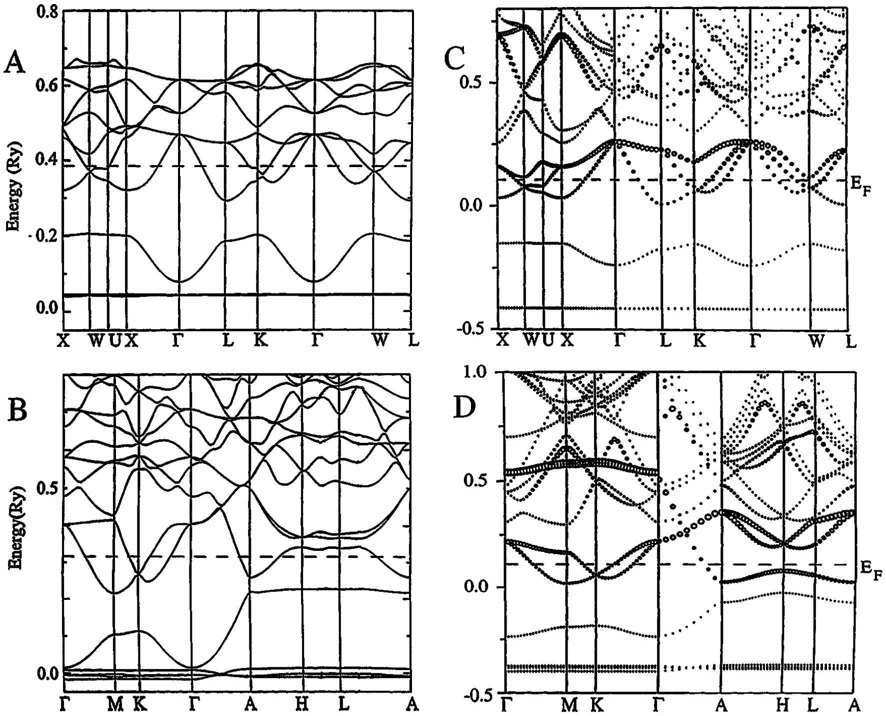

FIG. 1. The valance band structures of (A) K_2Ag and (B) K_3Ag and of the corresponding hypothetical structure (C) $\square_2Ag$ and (D) $\square_3Ag$ with the K atoms removed. The Fermi levels (horizontal dashed line) of the hypothetical structures $\square_2Ag$ and $\square_3Ag$ have been adjusted to account for the extra electrons donated by the K atoms. The size of the circles shown in the $\square_2Ag$ and $\square_3Ag$ band structures is proportional to the degree of contribution of the Ag $5p$ orbital to the band. The lowest energy flat bands are predominantly Ag $4d$. The next higher energy bands are mostly Ag $5s$ and the bands near the Fermi level have significant Ag $5p$ character (see text). Please note the energy scales are different for the four band structures.

not contribute appreciably to the occupied energy levels and have no significant effects on the bonding with and between the Ag atoms. This behavior of the electronic energy bands is consistent with Zintl's description [9] of alloy structures where in the K-Ag intermetallic phases there is almost complete electron transfer from K to Ag, completely filling the Ag $5s$ bands and partially occupying the Ag $5p$ bands. The K-Ag alloy structures can be described as a collection of K^+ situated within a negatively charged Ag framework with the effective electronic configuration for the Ag atom in K_2Ag as $4d^{10}5s^25p^1$ and $4d^{10}5s^25p^2$ in K_3Ag which is similar to the valence electron configuration for the Tl and Pb atoms, respectively. The significance of this analogy will be exemplified below.

In spite of the long Ag-Ag separation, directional Ag-Ag bonding is evident from the large energy dispersion in the Ag valence bands in these alloys. For example, in K_2Ag the Ag $5s$ band dispersion along the Γ-L direction (Fig. 1A), which in real space corresponds to the direction of the long Ag-Ag bonds, is 0.1 Ry. More unexpectedly, even larger energy dispersion (ca. 0.2 Ry) is observed in the next three partially occupied higher energy bands near the Fermi level with predominantly Ag $5p$ character along the directions of the extremely long Ag-Ag bonds. Significant band dispersion is also observed in the electronic band structure of K_3Ag and the hypothetical $\square_2Ag$ and $\square_3Ag$ structures. Thus, the charge transfer from K to Ag provides electrons to occupy diffuse Ag $5p$ orbitals which is the foundation for the structural stability of the K-Ag alloys.

Structural stability can be related to the moments of the electronic density of states (DOS) [11–13]. A topological analysis of structural motifs and their relationship to the structural stability can be performed by the method of moments analysis within the variance scaling tight binding Hamiltonian [12,14] model. The principle of moment analysis is based on the fact that the electronic energy of a crystal is related to contributions from structural motifs of the local bonding through the moments expansion of the DOS [15,16]. This powerful technique has been successful in providing a theoretical basis for the Hume-Rothery rules for alloy stability [16]. If the structures of elemental Ag, K_2Ag, and K_3Ag are examined from a different perspective, a common structural motif of hexagonal Ag sheets becomes apparent. In elemental Ag the hexagonal plane with $\ldots ABCABC \ldots$ stacking is easily recognized when the structure is viewed down the [111] axis. In K_2Ag (Fig. 2) the hexagonal layers expand to accommodate the K^+ and are shifted by $\frac{1}{3}$ unit cell along the [110] direction in a $\ldots AAA \ldots$ stacking. In K_3Ag (Fig. 2), more K is intercalated and the hexagonal Ag lattice planes expand further and shift back by $\frac{1}{3}$ unit cell along the [110] direction and stack in a $\ldots ABCABC \ldots$ manner resulting in a structure close to elemental Ag. These similarities strongly suggest that the

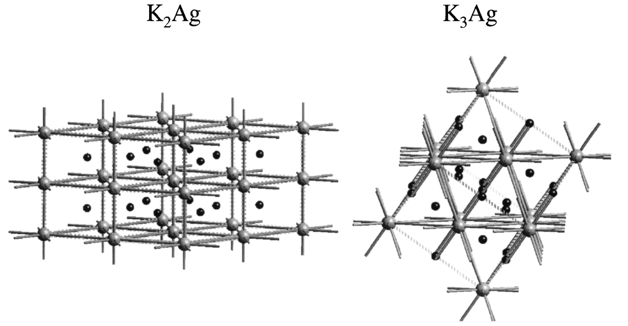

FIG. 2. The structures of K$_2$Ag and K$_3$Ag, indicating the hexagonal sheets of Ag atoms (large spheres) and intercalated K atoms (small spheres). In K$_2$Ag, the crystal axes system is hexagonal with the **c** axis along the short Ag-Ag bond; the **a**, **b** axes lie on the hexagonal Ag sheet. K$_3$Ag has a cubic unit cell. As shown in the figure, the hexagonal sheets lie perpendicular to the [111] direction and the dashed lines indicate the unit cell.

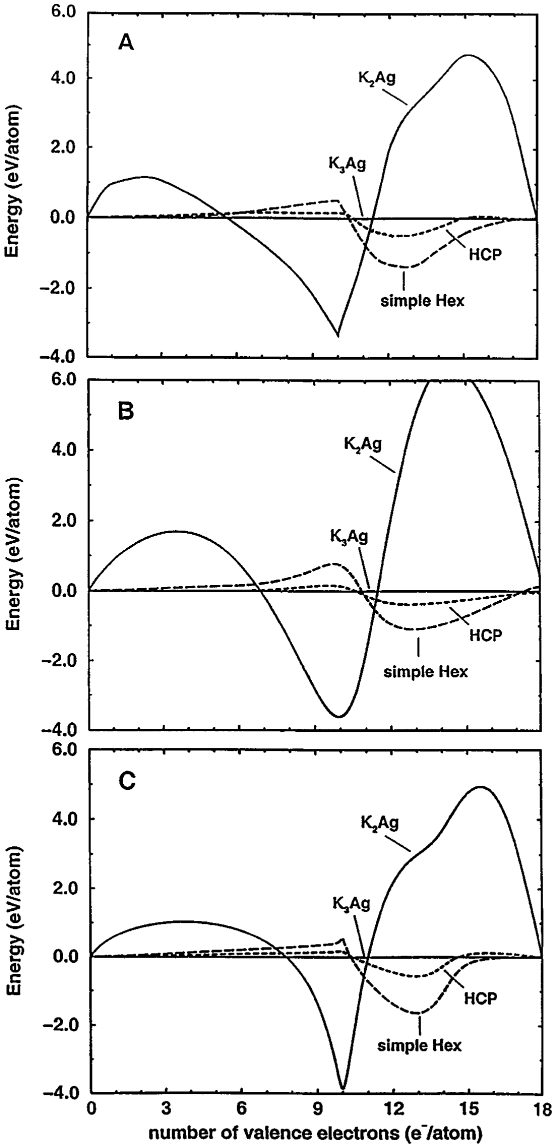

FIG. 3. Differences in energy between the structure types for K-Ag alloys and the reference structure (horizontal line at zero energy) of the fcc Ag sublattice of K$_3$Ag as a function of the number of valence electrons per Ag atom. The convention is that the curve with the most positive value corresponds to the most stable structure for that particular number of valence electrons per Ag atom. In (A) all moments are included; in (B) and (C) contributions from continued fraction expansions up through to fourth and sixth moments, respectively, are included.

fundamental building blocks of the crystal structures of the two alloys are intimately related and can be viewed as different stackings of the hexagonal Ag sublattices with K$^+$ ions intercalated between them (Fig. 2). This empirical evidence indicates that there is an inherent electronic preference for the formation of the basic structural unit that controls the stability. To test this hypothesis, the total electronic energy differences obtained from tight binding calculations on the Ag sublattices of K$_2$Ag and K$_3$Ag in the experimental geometry, as well as hypothetical hcp and a simple hexagonal Ag structure with all the Ag-Ag bonds set to 5.54 Å, are compared as a function of the number of electrons filling the valence orbitals of a Ag atom. Only the Ag framework atoms need to be considered explicitly in these calculations. As shown by the first-principles calculations, the K$^+$ ions transfer almost all the valence electrons to Ag. Consequently, the effective valence electron count for the Ag atoms in the sublattice are 13 e^- and 14 e^- per Ag atom for K$_2$Ag and K$_3$Ag, respectively. The curves relative to the fcc Ag sublattice of K$_3$Ag as a function of the band filling (number of electrons on each Ag atom) are shown in Figs. 3A–3C. The energy difference curves shown in Fig. 3A are the exact result computed directly from the total electronic density of states. To interpret this result in terms of structurally meaningful quantities, the energy difference curve is reconstructed from the contributing lower moments from a continued fraction expansion technique [14,15]. In Fig. 3B energy terms associated with the third and fourth moment of the DOS and the upper and lower energy bound of the valence band are included [15]. The third moment is related to the triangular arrangement of the Ag atoms within a given structure and the fourth moment is related to the number of squares as well as bond angles. The fifth and sixth moments, which are related to, among other things, the number of pentagons and hexagons, respectively, are included in Fig. 3C. We first examine the energy difference curve associated with the K$_2$Ag lattice. The profile of the energy difference curve is indicative of structural elements that are contained within the fourth moment of the DOS. The curve in Fig. 3B confirms this assertion. The large fourth moment (approximately 1.4 times that of K$_3$Ag) which arises from the presence of the short 3.60 Å Ag-Ag bond in the K$_2$Ag structure stabilizes this phase for electron counts above 12 e^-/atom. One may then be tempted to suggest that the theory would also predict that the K$_3$Ag structure should have a Ag sublattice as in K$_2$Ag. However, this is not viable because the Ag sublattice in K$_2$Ag is too compact to accommodate three K$^+$ ions. The interlayer spacing between the Ag planes must expand by at least 1.5–2.0 Å (the ionic radius of K$^+$) along the **c** direction to incorporate the additional K^+. The stretching of the short Ag-Ag bonds diminishes the large fourth moment effect and results in a structure closely resembling a simple hexagonal lattice. This structure is less stable than the fcc structure at an electron count of 14 $e^-/$atom appropriate for K_3Ag (Figs. 3A and 3C). Analysis of the shape of the energy difference curve shows that the energy lowering can be attributed to a smaller third moment (approximately 10% smaller than that of K_3Ag) of the simple hexagonal structure and has too few triangular faces for it to be stable above 10 $e^-/$atom relative to the fcc phase. An alternative to the $\ldots ABC \ldots$ fcc stacking of the hexagonal Ag sheets is the $\ldots ABAB \ldots$ hcp stacking. This structure, however, is less stable than the fcc packing at an electron count of 14 $e^-/$atom. The electronic origin of this is due to the fifth and sixth moments because of the close similarity between the topology of these two phases. This is indicated by the convergence in the crossover points of the energy difference curves only after the inclusion of the sixth moment (Fig. 3C) in the continued fraction expansion. The moment analysis demonstrates that the actual structure type which these phases adopt is primarily governed by the electronic structure of the Ag sublattice which depends on the effective number of valence electrons on the atom. The topologies of the Ag sublattices in K_2Ag and K_3Ag are remarkably similar to the structures of elemental Tl (hcp) and Pb (fcc), respectively.

The anomalously long Ag-Ag and very short K-K separations in the observed K-Ag structures can now be rationalized. Owing to the large mismatch in the ionic radii, in order to accommodate the large number of K^+, the Ag sublattice must expand while maintaining the structural integrity. This is possible only because of the spatially extended Ag $5p$ orbitals which preserve efficient Ag-Ag overlap at large separation. The unusually short K-K distances observed in the K-Ag alloys is a consequence of the formation of K^+ leaving a much smaller ion core. The smaller compressibility of K^+ in the solid at high pressure leads to short K-K distances. An *ab initio* calculation on a ${K_2}^{2+}$ dimer [17] shows that the repulsion energy is indeed smaller than the neutral K_2 dimer at short distances. A simple physical mechanism for the formation of the K-Ag bonding can now be proposed. The role of pressure is to compress the K atoms to a point where the charge transfer to Ag becomes favorable. The elemental Ag fcc framework must expand due to increased electron density on Ag atoms and to intercalate the K^+ ions. The structural progression from elemental Ag to K_2Ag and then to K_3Ag can be logically deduced.

Several important physical aspects of alloying at high pressure have been established here. First, there is no K $s \rightarrow d$ transition in K-Ag alloys; second, Miedema's rules are satisfied for high pressure alloys; third, Zintl's description is valid; fourth, the stability of the K-Ag alloy structure is primarily governed by the Ag sublattices; and, finally, the stability of the Ag sublattices is related to the effective number of valence electrons on the Ag atoms. The model presented here will have potential important applications for the understanding of the bonding and structure of high pressure alloy phases.

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